Environmental Effects of Dredging
Technical Notes

The K_{oc} of Nonpolar Organic Compounds in Sediment

Purpose

This technical note describes testing conducted to determine the partitioning of contaminants between sediment organic carbon and sediment interstitial water, assess the effects of sediment organic carbon upon K_{oc} of selected PCBs and fluoranthene, and investigate the effect of time of contact between contaminants and sediment upon the value of K_{oc}.

Background

The U.S. Environmental Protection Agency is authorized to develop and implement sediment quality criteria (SQC) under section 304(a) of the Clean Water Act. SQC, when promulgated, will profoundly affect U.S. Army Corps of Engineers (USACE) dredging and disposal operations. Aquatic disposal of dredged material and selection of aquatic disposal sites will be based on SQC. Most SQC approaches currently under development involve a determination of the relationship between contaminant concentrations in sediment and biological effects on organisms exposed to the contaminated sediment. The USACE is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as contaminant levels and effects in aquatic organisms. Knowledge of these interactions will provide the Corps with a means of evaluating the adequacy of proposed SQC approaches for estimating the potential impacts of dredged material disposal.

Additional Information

Contact the authors, Dr. James M. Brannon, (601) 634-3725, Dr. Judith C. Pennington, (601) 634-2802, Ms. Charolett Hayes, AScI Corp., (601) 638-1372, or Mr. Victor McFarland, (601) 634-3721, or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624.

Introduction

Sediment organic carbon has been identified as the most important factor controlling partitioning of nonpolar organic contaminants between sediment and water (Karickhoff 1981). Studies have also shown that partitioning of nonpolar organic compounds is strongly related to the octanol-water partitioning coefficient of the compound (Karickhoff 1981). Sediment concentrations expressed on a total organic carbon (TOC) basis have been used to predict concentrations of nonpolar organic compounds in sediment pore water for use as sediment quality criteria by the U.S. Environmental Protection Agency (EPA) (Brannon and others 1990).

The EPA approach for predicting interstitial water concentrations is called the Equilibrium Partitioning (EP) approach. The EP approach allows estimation of the concentration of a contaminant in interstitial water from sediment contaminant concentrations normalized to organic carbon. The calculated interstitial water concentrations are then compared to water quality criteria. If the predicted sediment interstitial water concentration for a given contaminant exceeds its chronic water quality criterion, the sediment is categorized as contaminated (Brannon and others 1990).

Prediction of pore-water contaminant concentrations based on values of K_{oc} (derived from K_{ow}, the octanol/water partition coefficient), total organic carbon content, and total contaminant concentration is likely to be incorrect. Measured pore-water concentrations have been shown to differ significantly from predicted values (Brannon and others 1991 and Steinberg, Pignatello, and Sawhney 1987). These differences can result from lack of equilibrium in the system or from factors related to organic matter composition (Gauthier, Seitz, and Grant 1987, Grathwohl 1990, Whitehouse 1985, and Schrap and Opperhuizen 1989) or other sediment factors affecting sorption capacity (Mingelgrin and Gerstl 1983). The source of organic matter affects the partitioning behavior of nonpolar organic compounds and can result in large variability in measured values of K_{oc}. Gauthier, Seitz, and Grant (1987) reported that K_{oc} can vary by a factor of 10 as a function of organic carbon aromaticity.

The laboratory experiments described in this technical note were designed to examine the relationships between sediment organic carbon and sediment interstitial water, the effects of sediment organic carbon on K_{oc} of selected polychlorinated biphenyls (PCBs) and fluoranthene, and the effects of time of contact between contaminants and sediment on interstitial water partitioning.

Materials and Methods

Three sediments of varying TOC content were used in this study — Hamlet City Lake sediment (9.0 percent TOC) from Hamlet, North Carolina; U.S. Army Engineer Waterways Experiment Station (WES) reference soil (silt) (0.5 percent TOC) from Vicksburg, Mississippi; and sediment from Brown's Lake (2.8 percent TOC), a freshwater lake in Vicksburg, Mississippi. These sediments were

amended with 10 μg of either radiolabeled PCB 52 (2,2′,5,5′-tetrachlorobiphenyl-UL-^{14}C), PCB 151 (2,2′,3,5,5′,6-hexachlorobiphenyl-UL-^{3}H), or fluoranthene (3-^{14}C-fluoranthene) per g dry sediment weight using methods described previously (Brannon and others 1989). Sample bottles containing the sediments were stored upright to allow the sediments to settle and maintain a water cover. Samples were incubated for up to 180 days, with samples taken at intervals. At all sampling periods, concentrations of free and bound PCB 52, PCB 151, and fluoranthene were determined in the interstitial water using reverse phase partitioning (Landrum and others 1984).

Results and Discussion

Interstitial Water

Concentrations of free contaminants in interstitial water generally decreased or remained constant over time (Figure 1), even though the fraction of bound contaminant (contaminant complexed with dissolved organic carbon and microparticulates) remained essentially constant. For this reason, average values rather than time-dependent values of the bound contaminant fraction are given (Table 1). Decreases in concentrations of free contaminant are consistent with movement of nonpolar organic contaminants into interparticle organic matter pores over time (Brusseau and Rao 1989), resulting in decreased interstitial water concentrations.

Table 1. Average (Standard Error) Fraction of Bound Contaminant in
Interstitial Water during 180 Days of Testing

Contaminant	Brown's Lake	Hamlet City	Silt
PCB 151	0.34 (0.03)	0.36 (0.02)	0.29 (0.03)
PCB 52	0.05 (0.009)	0.08 (0.02)	0.04 (0.004)
Fluoranthene	0.16 (0.03)	0.04 (0.004)	0.05 (0.017)

Contaminant K_{oc} Values

The ability of EP to predict interstitial water PCB 52, PCB 151, and fluoranthene concentrations in sediment was tested by comparing estimated K_{oc} with measured K_{oc} values. K_{oc} is the partition coefficient for sediment organic carbon and is one of the key components used in EP for predicting interstitial water concentrations. Estimated K_{oc} values were computed by substituting values of log K_{ow} (octanol/water partition coefficient) for fluoranthene (5.5) (Tetra Tech 1985), PCB 52 (5.84), and PCB 151 (6.64) (Hawker and Connell 1988) in Equation 16 from Karickhoff (1981) that relates K_{ow} to K_{oc}. These calculations resulted in estimated K_{oc} values of 5.09, 5.43, and 6.22 for fluoranthene, PCB 52, and PCB 151, respectively. Measured values of K_{oc} were determined by dividing the TOC normalized sediment concentration of PCB
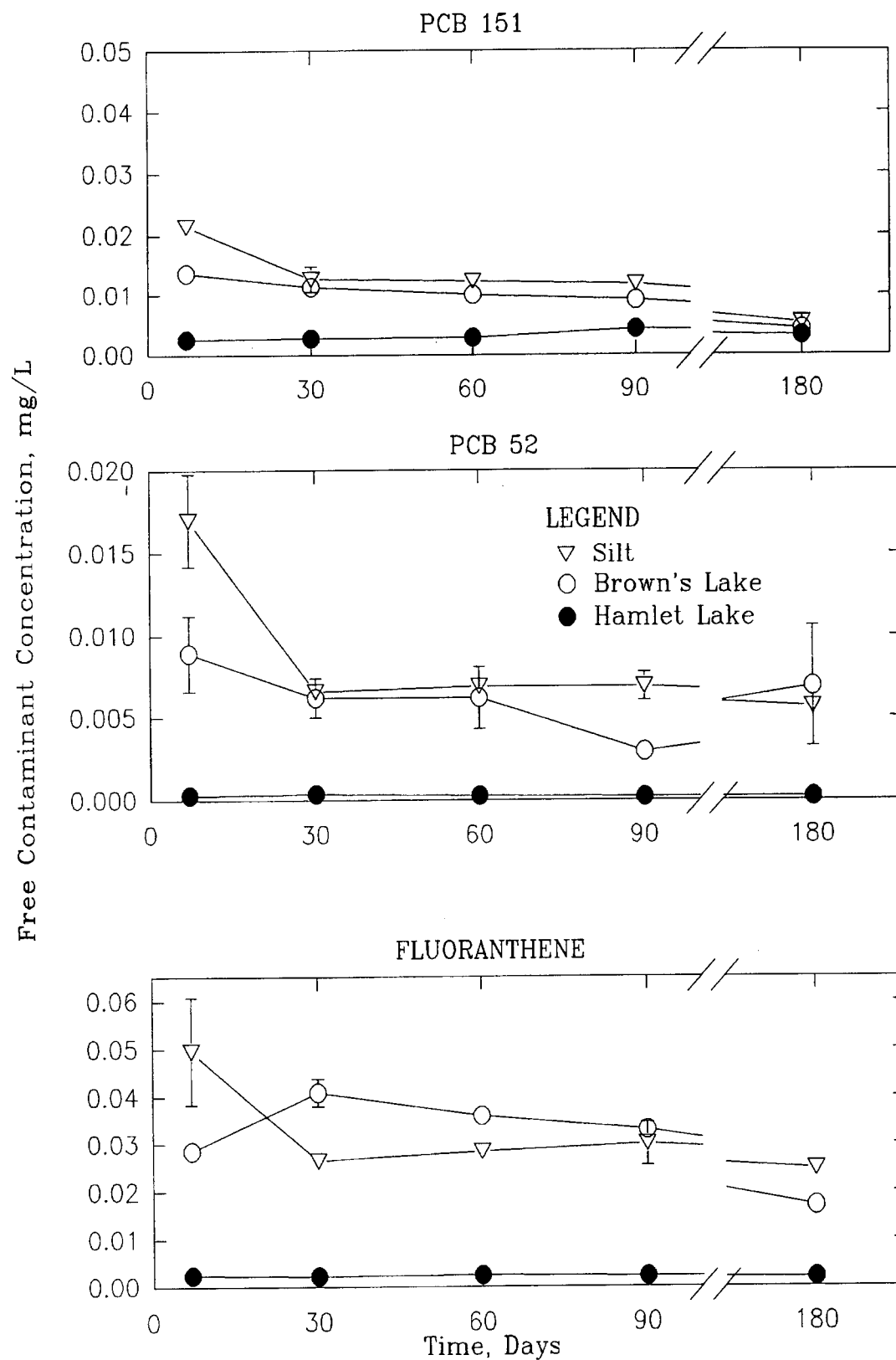
Figure 1.   Concentrations of free PCB 151, PCB 52, and fluoranthene in interstitial water

52, PCB 151, or fluoranthene by the free interstitial water concentration of the respective compounds.

Measured log K_{oc} values for PCB 151 ranged from approximately 4.2 to 4.9 and did not vary greatly between sediments (Figure 2). Furthermore, log K_{oc} values for PCB 151 generally increased as exposure time in the sediment increased. Measured values of log K_{oc} for PCB 151 were considerably lower than the estimated value.

Measured values of log K_{oc} for PCB 52 and fluoranthene were in relatively close agreement for silt and Brown's Lake sediment, but were considerably higher (0.5-0.9 log units) in Hamlet Lake sediment (Figure 2). Measured values of log K_{oc} for PCB 52 generally increased over time, similar to the results for PCB 151. Measured values of log K_{oc} for PCB 52 were generally lower than the estimated value of log K_{oc}, except for Hamlet Lake sediment, which was slightly higher. Measured values of fluoranthene log K_{oc} generally increased over time and were lower than the estimated value, at times by as much as a full log unit.

Measured log K_{oc} decreased as sediment TOC content decreased for PCB 52 (Figure 3). Fluoranthene log K_{oc} varied in the same manner as did PCB 52 until TOC reached 2.8 percent, when no further change was noted. PCB 151 varied only slightly with sediment TOC. Ideally, measured values of log K_{oc} should remain constant as TOC changes if EP reliably predicts free interstitial water concentrations of nonpolar organic contaminants. This situation was observed only for PCB 151. The deviation of measured K_{oc} values from estimated values and the dependence of measured PCB 52 and fluoranthene K_{oc} values on sediment TOC concentrations indicate that predictions of free interstitial water contaminant concentrations from EP are not reliable for all compounds. This may result from factors such as clay content and clay species increasing the sorption capacity of the sediment over that of the organic matter, resulting in a decrease in measured K_{oc}.

Summary of Findings

Changes in K_{oc} over time and among sediments depended upon the compound tested. Values of K_{oc} measured using free interstitial water concentrations did not agree with estimated K_{oc} for all compounds and in all sediments. Estimated values of K_{oc} were generally substantially higher than measured values of K_{oc}. This was especially true of PCB 151 and fluoranthene in all sediments tested. For PCB 52, PCB 151, and fluoranthene, K_{oc} also generally increased as incubation time increased, indicating that sorption processes that reduced the free concentration of these compounds in the interstitial water were continuing. PCB 52 and fluoranthene K_{oc} also showed a marked dependence on sediment TOC concentration, generally decreasing as sediment TOC decreased.
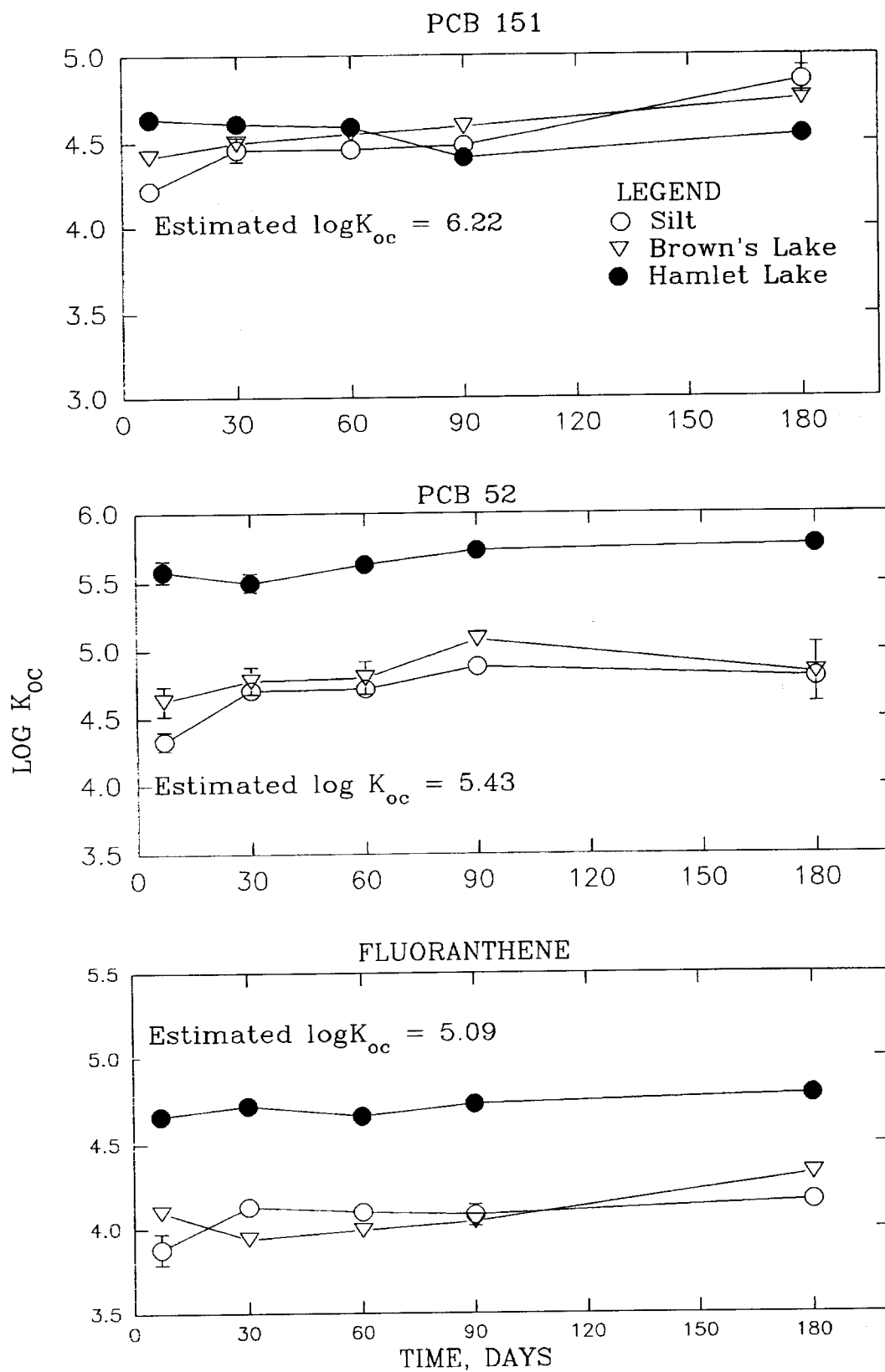
PCB 151

Estimated $\log K_{oc} = 6.22$

LEGEND
○ Silt
▽ Brown's Lake
● Hamlet Lake

PCB 52

LOG K_{oc}

Estimated $\log K_{oc} = 5.43$

FLUORANTHENE

Estimated $\log K_{oc} = 5.09$

TIME, DAYS

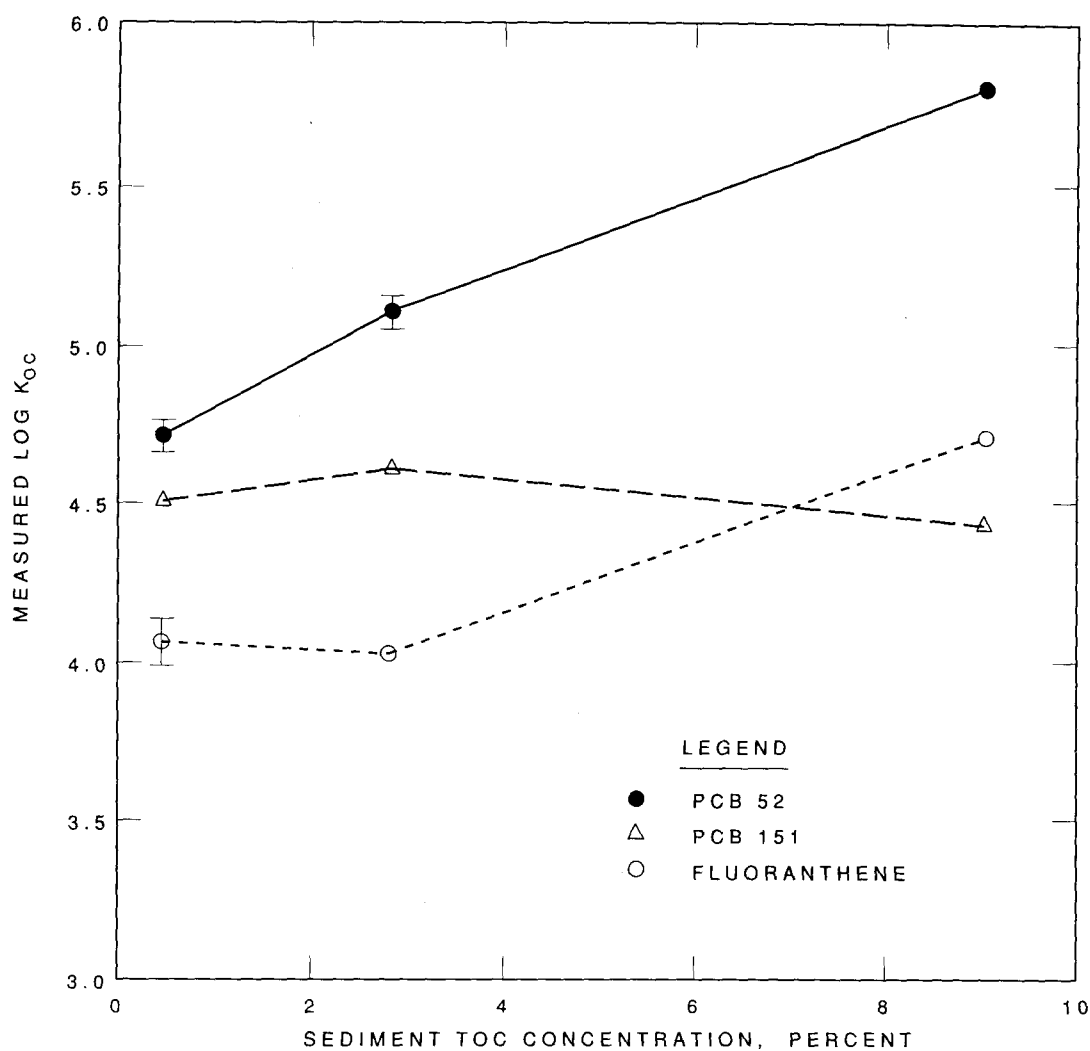Figure 2.   Measured log K_{oc} for PCB 151, PCB 52, and fluoranthene

Figure 3. Measured log K_{oc} following three months incubation as a function of sediment TOC

The data indicated that a high degree of uncertainty exists for K_{oc} values among sediments and compounds. This can result in either overestimation or underestimation of free interstitial water contaminant concentrations when using equilibrium partitioning, estimated K_{oc} values, and TOC. Predictive methods with a high degree of uncertainty are not good regulatory tools. The factors affecting K_{oc} must be better understood before rigid regulatory criteria are promulgated.

References

Brannon, J. M., McFarland, V., Pennington, J. C., Price, C. B., and Reilly, F. J., Jr. 1989. "Procedures for Examining the Relationship Between Sediment Geochemistry and Biological Impacts of Contaminants," *Environmental Effects of Dredging Technical Notes* EEDP-04-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Brannon, J. M., McFarland, V. A., Wright, T. D., and Engler, R. M. 1990. "Utility of Sediment Quality Criteria (SQC) for the Environmental Assessment and Management of Dredging and Disposal of Contaminated Sediments," Seminar Proceedings No. 22, Coastal and Inland Water Quality, R. G. Willey, ed., U.S. Army Corps of Engineers, Committee on Water Quality, Washington, DC, pp 7-19.

Brannon, J. M., Price, C. B., Reilly, F. J., Jr., Pennington, J. C., and McFarland, V. 1991. "Interim Results: The Relationship Between Sediment Organic Carbon and Biological Uptake of Contaminants," *Environmental Effects of Dredging Technical Notes* EEDP-01-25, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Brusseau, M. L. and Rao, P. S. C. 1989. "Sorption Nonideality during Organic Contaminant Transport in Porous Media," *CRC Critical Reviews in Environmental Control*, Vol 19, pp 33-99.

Gauthier, T. D., Seitz, W. R., and Grant, C. L. 1987. "Effects of Structural and Compositional Variations of Dissolved Humic Materials on Pyrene K_{OC} Values," *Environmental Science and Technology*, Vol 21, pp 243-248.

Grathwohl, P. 1990. "Influence of Organic Matter from Soils and Sediments from Various Origins on the Sorption of Some Chlorinated Aliphatic Hydrocarbons: Implications on K_{OC} Correlations," *Environmental Science and Technology*, Vol 24, pp 1,687-1,693.

Hawker, D. W., and Connell, D. W. 1988. "Octanol-Water Partition Coefficents of Polychlorinated Biphenyl Congeners," *Environmental Science and Technology*, Vol 22, pp 382-387.

Karickhoff, S. W. 1981. "Semi-empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils," *Chemosphere*, Vol 10, pp 833-846.

Landrum, P. F., Nihart, S. R., Eadie, B. J., and Gardner, W. S. 1984. "Reverse Phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters," *Environmental Science and Technology*, Vol 18, pp 187-192.

Mingelgrin, U., and Gerstl, Z. 1983. "Reevaluation of Partitioning as a Mechanism of Nonionic Chemicals Adsorption in Soils," *Journal of Environmental Quality*, Vol 12, pp 1-11.

Schrap, S. M., and Opperhuizen, A. 1989. "Quantifying the Sorption of Organic Chemicals on Sediments," *Chemosphere*, Vol 18, pp 1,883-1,893.

Steinberg, S. M., Pignatello, J. J., and Sawhney, B. L. 1987. "Persistence of 1,2-Dibromoethane in Soils: Entrapment in Intraparticle Micropores," *Environmental Science and Technology*, Vol 21, pp 1,201-1,208.

Tetra Tech. 1985. "Bioaccumulation Monitoring Guidance; 1, Estimating the Potential for Bioaccumulation of Priority Pollutants and 301(h) Pesticides

Discharged into Marine and Estuarine Waters," Final Report prepared by Tetra Tech, Inc., for the U.S. Environmental Protection Agency Under Contract No. 69-01-6938.

Whitehouse, B. 1985. "The Effects of Dissolved Organic Matter on the Aqueous Partitioning of Polynuclear Aromatic Hydrocarbons," *Estuarine, Coastal Shelf Science,* Vol 20, pp 393-402.